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Hydrogen Cyanide Emissions from a Three-way Catalyst Prototype

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HYDROGEN CYANIDE EMISSIONS FROM A THREE-WAY CATALYST PROTOTYPE

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16. ABSTRACT

Four catalysts, nominally identical except for Pt/Rh ratio, were tested for emissions of regulated pollutants and for HCN, NH_3, $SO_4^=$ and H_2S. Fuel economy was also measured. The tests were conducted over the FTP, CFDS, and 64 and 80 kph cruise modes, using three simulated malfunction modes: O_2 sensor disconnected-idle adjustment correct; O_2 sensor disconnected-idle adjustment enriched; 13% misfire. The catalysts were prepared by Engelhard Industries under conditions similar to those used in making commercial three-way catalysts. A prototype Volvo TWC vehicle was the test car. The four catalysts contained respectively: Rh only, 17% Rh-Pt; 5% Rh-Pt; Pt only. Tests were also run with no catalyst under the malfunction modes and with each catalyst under normal engine conditions. Of the fifteen possible test combinations (four catalysts and no catalyst x 3 malfunction modes), twelve were chosen to be run, with four replicates, giving sixteen runs total.

No HCN was detected at the tailpipe under normal operating conditions over the FTP. However, under the malfunction modes, HCN emissions were generally found. During the FTP and CFDS cycles all of the catalysts appeared to remove some HCN from the exhaust gas under all malfunction modes, but during cruise some catalysts under certain malfunctions caused a further increase in tailpipe HCN emissions. The maximum level observed was about 40 mg/km.

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1. Summary

The research described in this report was conducted under EPA Contract No. 68-03-2485. It consisted of testing four catalysts, nominally identical except for Pt/Rh ratios, for their emission levels of regulated gaseous pollutants as well as the unregulated pollutants HCN, NH_3, $SO_4^=$ and H_2S during simulated three-way catalyst vehicle malfunction modes. Fuel economy measurements were also made. The catalysts were each tested under Federal Test Procedure (FTP) and Congested Freeway Driving Schedule (CFDS) cycles, 64 and 80 kph cruises, and at idle. The simulated malfunction modes were:

1) O_2 sensor disconnected - idle adjustment correct
2) O_2 sensor disconnected - idle adjustment enriched
3) 13% misfire

The catalysts were prepared by Engelhard Industries under conditions similar to those used in manufacturing the three-way catalyst used in Volvo TWC automobiles. A prototype of this vehicle was used as the test car.

Of the fifteen possible test conditions (four catalysts and no catalyst x three simulated malfunction modes), it was decided to run only twelve conditions and replicate four of these, providing a total of sixteen run sequences, each sequence consisting, as mentioned, of the FTP, CFDS, 64 and 80 kph cruise, and idle. The replicates allowed calculation of the standard deviation of measurement for the various pollutants looked at.

HCN

Normal operation of the catalysts, under FTP conditions, showed no HCN tailpipe emissions, at least to the detectability limits for this cycle of 1.4 mg/km. However, under malfunction conditions, HCN emissions were generally observed. During malfunction, for the cyclic FTP and CFDS runs, the highest levels were found for the no-catalyst case, indicating that HCN was produced upstream of the catalyst bed. It is not known, however, whether this occurred in the combustion chamber or in the exhaust system. In any case, when catalyst beds were present, tailpipe emissions of HCN were invariably lower, indicating that, at least under cyclic driving modes, all the catalysts tested were actually removing HCN from the exhaust gas.

A different situation was observed under steady state malfunction test conditions. The 100% Rh catalyst appeared to produce HCN in the exhaust gas when the O_2 sensor was disconnected, with the idle adjustment maintained correct. Under these conditions, the other catalysts removed HCN, as in the cyclic driving modes. When the idle

adjustment was enriched, the 100% Rh catalyst produced still more HCN, and even the 6% Rh catalyst now made HCN. Under this condition, only the 100% Pt catalyst continued to remove HCN.

At misfire, all catalysts removed HCN from the exhaust, although there seems to be a correlation between catalyst Rh content and tailpipe emission level.

NH_3

Ammonia emission levels were much higher under malfunction conditions than under normal operating conditions. Although all four catalysts showed this trend, the pure Rh gave the highest levels, which appeared to increase with degree of enrichment. The highest single value, 724 mg/km, was observed under misfire conditions, however. At idle, NH_3 emission levels were quite low under all catalyst-malfunction combinations.

CO

Generally, for the two sensor-disconnected malfunction modes the pure Rh catalyst provided the most control, with the pure Pt worst. For example, under FTP conditions, the 100% Rh catalyst removed about 50% of the CO, giving levels of 10-24 g/km. The 100% Pt catalyst also removed about 50% of the CO when the idle was correctly set, but none when the idle was enriched. In no case, however, did the conversion efficiency approach the levels achieved during normal operation, where emissions ranged around 2 gm/km. Under misfire conditions, all four catalysts were generally equivalent, giving about 40-70% conversion efficiency.

HC

Under misfire conditions the pure Pt catalyst was invariably most efficient for HC removal, and the pure Rh the least. However, under the O_2 sensor disconnect modes the situation was more complex. The pure Pt was the worst catalyst under FTP and cruise conditions, but, for the CFDS was the best catalyst when the idle adjustment was properly set. Under idle enrichment, the Rh-containing catalysts were again best, however. HC emission levels were generally much higher for malfunction modes than during normal operation, although the best of the malfunction runs equalled the normal runs. At idle little, if any, HC conversion was achieved, except under the misfire mode, where perhaps 75% control was seen.

NO_x

Comparing FTP results for the O_2-sensor disconnect modes with the emissions during normal operation, it is seen that pure Rh is still the most effective catalyst for NO_x removal. However, its activity does

not appear as great, especially when the idle is correctly adjusted. The Pt catalyst was about the same in activity under normal and O_2-sensor disconnect modes. The pure Rh catalyst was also the best under CFDS and cruise conditions, with the pure Pt worst. At misfire and idle conditions, NO_x tailpipe emissions were extremely low with all catalysts.

$SO_4^=$

Sulfate emissions were low under all conditions tested, in no case exceeding 3.9 mg/km. For the two sensor disconnect conditions, the pure Pt catalyst seemed to produce some $SO_4^=$, compared to raw engine exhaust valves, while the pure Rh catalyst removed $SO_4^=$ from the raw exhaust. Under misfire conditions the situation was reversed between the two catalysts.

H_2S

Under normal operating conditions a maximum value of 0.3 mg/km was observed for H_2S. Under malfunction conditions increased values were observed, although in no case did the level exceed about 8 mg/km, this during misfire. Under O_2 sensor disconnect conditions, values no higher than about 3 mg/km were seen. No correlation with catalyst composition was apparent.

II. Introduction

In 1975 a report was published by Voorhoeve, et al., showing that HCN could be formed over a platinum automotive exhaust oxidation catalyst in the laboratory when the catalyst was exposed to synthetic mixtures of NO, CO and H_2 in He at temperatures from 400 to 800°C.(1) It was also found that the presence of small amounts of H_2O or SO_2 severely suppressed HCN formation. Because of the presence of NO, CO and H_2 in automotive exhaust and the similarity between the laboratory catalytic and temperature conditions with those observed in vehicles, along with the high toxicity level of HCN, several studies have been carried out to confirm the initial laboratory results and to determine if HCN can be formed in real automotive exhaust gases. In some unpublished work done at Exxon Research and Engineering Company a laboratory mixture of CO, NO, C_3H_8 and H_2, forced over a PTX-IIB automotive catalyst at 700°C, yielded a similar level of HCN to that reported by Voorhoeve. However, when gas mixtures simulating lean and rich exhaust gases were passed over the same catalyst, the former yielded no detectible HCN and the latter only around 1 ppm, compared to levels of up to 700 ppm observed with the less realistic gas mixtures. To extend this work to actual exhaust gases, a 1975 car, equipped with a 350 C.I.D. engine and a Pt-Pd pelleted catalyst, was run under FTP and 64 kph cruise conditions with the catalyst fresh and aged and under normally lean as well as rich carburetion. In no case did the HCN emissions exceed 3 mg/km, or the equivalent of about 1.5 ppm in the exhaust gas.

Shortly after this work was completed, indicating that HCN formation should not be a problem with conventional oxidation catalyst vehicles, even under abnormally rich operating conditions, the U.S. Environmental Protection Agency obtained some three-way catalyst vehicles. These were manufactured by Volvo and had previously been used for certification testing. Bradow and Stump of the EPA found that under normal stoichiometric air-fuel ratio, and lean malfunction operating conditions, no detectable HCN was formed.(2) However, when the system was adjusted to operate rich, easily detectable amounts of HCN were formed over the catalyst. At the request of the EPA, Exxon repeated these types of experiments, using similar, and, in one case an identical vehicle, to those used by the EPA. Our results basically confirmed those obtained by the EPA.

This raised the question of why, when exposed to rich exhaust gas, the three-way catalyst system produced HCN. In contrast, earlier Exxon work with a conventional oxidation catalyst vehicle, also exposed to a rich exhaust gas, did not find such an effect. A possible answer was catalyst composition, and part of this mystery was cleared up by additional EPA studies. Bradow and Stump tested a number of catalysts on an engine dynamometer stand, with the carburetor adjusted to yield a rich exhaust gas. It was found that rhodium-containing catalysts tended to give significantly higher levels of HCN than did Pt or Pt-Pd catalysts. Since the Volvo catalysts contained RH, and the catalyst

used by Exxon did not, these results appear to explain the discrepancy. They support also some earlier laboratory work at Imperial Chemical Industries, Ltd., which reported Rh to be a much more effective catalyst for the reduction of NO_x than is Pt, and further showed the reduction to be less selective to N_2 than in the case of Pt, at least at temperatures below 600°C(3)

Because of the implication of Rh and of rich operation in HCN formation, Exxon Research and Engineering undertook this program to study more closely the effects of catalyst Rh content and vehicle malfunction mode on the rate of HCN production from a three-way system vehicle. Also, because of the report of Bradow and Stump that high speed driving increased HCN formation, the effects of several different cyclic and steady-speed driving modes were investigated.

III. Experimental Conditions

III.1 Vehicle Description

The car used in this program was a prototype of the 1977 three-way system vehicle introduced by Volvo in California. It was loaned to us by Engelhard Industries Division, where it had been used for fleet testing. The car had accumulated approximately 27,000 km prior to this program. With the exception of routine maintenance and of catalyst changes, to be discussed in Section III.4, it was used as received.

III.2 Test Fuel

The test fuel contained 305 ppm S, < 0.0025 g/l of Pb and approximately 0.25 mg/l of P. The fuel was blended from unleaded components and the desired S content obtained by the addition of equal S-bearing amounts of thiophene and di-t-butyl disulfide. A complete inspection report of the fuel is given in Table III-1.

III.3 Test Sequence

III.3.1 Driving Modes

During each of the catalyst-system condition combinations, the vehicle was driven over the Federal Test Procedure, the CFDS, and one-half hour periods of 64 and 80 kph cruises and of idle. During each driving mode measurements of emissions of HC, CO, NO_x, HCN, NH_3, H_2S, and SO_4 were made. In addition, fuel economy was also determined.

III.3.2 Test Design

Instead of running each of the possible fifteen combinations of catalyst and system (four catalysts and no catalyst times three system conditions) it was felt to be more useful to omit several and replace them with some replicates of the remaining combinations. Accordingly, twelve of the possible combinations were actually run and four were replicated, making a total of sixteen test sequences. The final arrangement is shown in Table III-2.

III.4 Three-Way Catalysts

The four catalysts in this program were prepared by Engelhard Industries. Although the details of catalyst preparation and composition are proprietary to Engelhard, they were requested to make the catalysts in a manner similar to that used in producing the catalyst used commercially by Volvo in their 1977 three-way system vehicles being sold in California. All four catalysts were similar in such properties as substrate, geometry, and total noble metal content.

TABLE III-1

TEST FUEL BLEND

Research Octane, ASTM	93.5
Motor Octane, ASTM	84.0
Gravity, API @ 60°F	61.7
Breakdown Time, Minutes	960+
Sulfur, ppm	305
Phosphorous, mg/100 ml	0.025
Lead, g/gal	<0.01
FIA, Vol. %	
Aromatics	24.5
Saturates	63.1
Olefins	12.4
RVP, kPa	78.6 (11.4 psi)
Evap. @ °C	
38	5%
57	20%
101	50%
173	90%
Initial Boiling Point, °C	28
Final Boiling Point, °C	210

TABLE III-2

SUMMARY OF SIXTEEN TEST PROGRAM OF HCN EMISSIONS

Catalyst/ Operating Mode	100% Rh	Pt-17% Rh	Pt-5% Rh	100% Pt	None
O_2 sensor disconnected	XX*	-	X	X	X
O_2 sensor disconnected A/F enriched	X	-	XX	X	XX
Misfire	X	XX	-	X	X

* Double X indicates replicate.

Each catalyst was broken in under normal operating conditions for one day using the modified AMA cycle. Following this, FTP emissions for each catalyst were measured, again under normal operating conditions.

They differed only in noble metal composition. One catalyst contained Pt as the only noble metal component, another contained only Rh. The other two had Pt/Rh ratios of 83/17 and 94/6. An empty catalyst canister was used for the "no catalyst" runs.

III.5 Vehicle Malfunctions

Since the primary purpose of this program was to determine the HCN and NH_3 emissions of three-way system vehicles under abnormal operating conditions, three failure modes, considered typical of those which might occur in consumer use, were induced in the test car. Two of these involved O_2 sensor failure, with and without enrichment of the idle adjustment. The third was a random misfire simulating partial ignition failure.

III.5.1 O_2 Sensor Disconnected

III.5.1.1 Air-Fuel Ratio Enrichment

In this operating mode the O_2 sensor was disconnected, to simulate its total failure. In addition, the idle adjustment of the fuel injection system was set richer than normal. This provided substantial deviations from stoichiometry, as demonstrated by steady state measurements, shown in Table III-3.

Table III-3

Steady State Air-Fuel Ratios

O_2 Sensor Off-Idle Enrichment

Speed, km/h	Average A/F Ratio*	Range
idle	13.0	12.7-13.2
64	13.8	13.7-13.9
80	13.8	13.2-14.1

* Average of 4 runs.

It can be seen that in all cases the air-fuel ratios were substantially lower than the stoichiometric value of about 14.6. Although air-fuel ratios were not measured during cyclic operation, it is likely that their values remained below stoichiometric during these driving modes as well.

III.5.1.2 Air-Fuel Ratio Properly Set

In this malfunction mode the idle adjustment was set according to specifications. Thus the only vehicle malfunction was the sensor disconnection. It can be seen from Table III-4 that under these conditions the system more closely approached stoichiometric conditions than when the idle was misadjusted. However, air-fuel values were still rich.

Table III-4

Steady State Air-Fuel Ratios

O_2 Sensor Off-Normal Idle Adjustment

Speed, km/h	Average A/F Ratio*	Range
idle	14.1	14.0-14.2
64	14.4	14.3-14.5
80	14.4	14.3-14.5

* Average of 4 runs.

III.5.1.3 Induced Misfire

The third malfunction mode studied in this program was partial misfire. For this mode, the idle adjustment and O_2 sensor were operated normally, but a random misfire generator, developed at Exxon Research and Engineering Company, was used to randomly prevent plug firings, thereby simulating a poorly operating ignition system. Approximately a 13% misfire rate was used.

III.6 Chemical Analyses

III.6.1 HCN Analysis

The HCN content of the exhaust gas was determined by drawing a sidestream of the CVS diluted gas through a bubbler train. The flow rate was approximately 2 l/min. Generally three bubblers are used in series. The first contains dilute H_2SO_4, and is used for NH_3 sampling, to be described in Section III.6.2. The last two contain 80 ml. each of a solution made up of 50 ml. of 1N NaOH in deionized water and 30 ml. of deionized H_2O. The second of these bubblers, third in the train, is used as a precaution in the unlikely event that HCN is not completely trapped in the first NaOH bubbler. Other

precautions included the use of glass sampling lines wherever possible Short lengths of stainless steel are acceptable, but plastics, including Teflon, were avoided. Since water condensation may cause sampling losses, heated lines should be used if the gas stream is water saturated. Finally, H_2S may interfere with specific ion electrode detection of CN^-. Therefore, if H_2S is suspected, the sample solution should be treated with $Cd(OH)_2$ to precipitate sulfide prior to electrode analysis.

After gas sampling is completed the NaOH bubblers are worked up for analysis by emptying each one into a 100 ml. volumetric flask and adding deionized rinse water from the bubbler to make up 100 ml. total volume. A 20 ml. aliquot is pipetted from each solution in separate plastic containers. To each is added 1 ml. of 10N NaOH solution. Potential readings are then taken with a cyanide specific ion electrode according to the manufacturers instructions. If sulfide is suspected in the solution, add about 30 ml. of $Cd(OH)_2$ or Cd_2CO_3 solution, stir and filter before taking readings.

The cyanide solutions should be stirred at a constant rate during the potential reading, and values should be taken only after the potential stabilizes. The cyanide concentration of each scrubber solution is determined by comparing the potential reading with a calibration curve, made up as described in Appendix A. This appendix also contains further details of the cyanide analysis procedure. Appendix B presents the results of a brief study by George Milliman of the Analytical and Information Division of ERE on the effects of varying amounts of CO_2 passage through the bubbler solutions, and our method of counteracting any such effects, the responses of single and double junction reference electrodes, and a comparison of two brands of reference electrodes. Finally, Appendix C is an operating manual for one such specific CN^- ion electrode, offering a theoretical discussion of factors affecting electrode operation.

It should be noted that the first bubbler, containing dilute H_2SO_4, is also capable of trapping small quantities of HCN along with the intended NH_3. Therefore the solution from this impinger must also be analyzed for HCN and the results added to those from the two NaOH bubblers. The solution is worked up as described in Section III.6.2 and a 20 ml. aliquot taken. It is made strongly basic with 1 ml. of concentrated NaOH and analyzed in the same manner as the solutions from bubblers 2 and 3.

The limits of detectability for HCN using the above procedures was based on the lower limit of 0.04 µg CN^-/ml capable of detection in the original samples. With exhaust gas flow rates of 2 l/min and 80 ml of solution in each scrubber, a lower limit of 1.4 mg/km was obtained over the FTP. The 64 kph and 80 kph cruises gave 0.8 and 0.6 mg/km respectively for gas sampling periods of one-half hour.

III.6.2 NH_3 Analysis

The solution used in the impingers for NH_3 analysis is prepared by adding 1.1 ml of concentrated H_2SO_4 to a 1 litre volumetric flask and filling to the mark with deionized H_2O. The impinger is filled with 80 ml of this solution and after sampling, at 2 l/min, an additional 20 ml is used for rinsing and added to the first 80 ml in a volumetric flask to make a total of 100 ml of sample solution. Analysis with a gas sensitive NH_3 electrode is carried out on 20 ml aliquots of this sample according to the electrode manufacturer's instructions. Further details of this procedure are found in Appendix D. The limits of detectability of NH_3 were 6.5 mg/km over the FTP and 2 and 1.5 mg/km for the one-half hour cruises at 64 and 80 kph respectively.

III.6.3 Regulated Emissions

Determination of HC, CO, and NO_x emissions were carried out in the standard manner, using CVS bag samples and instrumental analyses. These included flame ionization detection for HC, non-dispersive IR for CO and chemiluminescence for NO_x. Details of the CVS unit can be found in a recent report prepared for the EPA by Exxon Research and Engineering Company[4].

III.6.4 Sulfate Emissions

Sulfate emissions were measured simultaneously with the H_2S, HCN, NH_3 and regulated emissions described in Sections III.6.1-3, using the Exxon exhaust particulate sampling system. Details of this system and of the analytical procedure used to measure sulfate collected on the sampling system filters may be found in Reference 4. The limits of detectability were 0.4 mg/km for the FTP and 0.3 mg/km for the other driving modes.

III.6.5 Fuel Economy

Fuel economy was determined by the carbon balance method, with the results checked by direct weighing of fuel before and after each run. A high degree of consistency was found both internally, in comparing successive runs where only the catalyst was changed, and between the carbon balance and weight methods. The fuel weight consumptions for each run and driving mode are given in Appendix E.

III.6.6 Hydrogen Sulfide Emissions

H_2S was determined by passing a known amount of exhaust gas, generally at 1 l/min, but on occasion at 2 l/min, through scrubbers containing a buffered zinc acetate solution. After sampling, solutions of formaldehyde, N,N-dimethyl-p-phenylene diamine sulfate in H_2SO_4, and ferric ammonium sulfate were added. Absorbance was measured at 667 nm and in 5 mm cells vs water. Total µg of H_2S were then determined by reference to a calibration curve. A more detailed discussion is found in Appendix F. Under FTP conditions, the detectability limit was 0.07 mg/km. For the CFDS it was 0.06 or 0.11 mg/km, depending on the exhaust gas flow rate. At cruise for one-half hour it was about 0.04 mg/km.

IV. Experimental Results

IV.1 Catalyst Comparisons Under Normal Operating Conditions

Prior to starting the test matrix comparing the various catalysts under three malfunction modes, the four catalyst formulations were each run on the Federal Test Procedure with the test vehicle set up for normal, stoichiometric operation. This served to establish a base case against which to compare the effects of the malfunctions and to determine the levels of the unregulated emissions HCN and NH_3 which could be expected from properly operating three-way systems. It also provides a measure of catalyst composition effects under normal operating conditions.

Table IV-1 gives the regulated and unregulated emissions, as well as fuel consumption, for these runs. No trend with catalyst composition is evident for HC, CO, HCN or $SO_4^=$ emissions, all of which are very low. Ammonia emissions are also low, especially compared to values observed in malfunction tests, as will be indicated in later sections. The pure Rh and Pt catalysts gave the highest values, but in view of the overall low levels it is not clear if this is significant. The most interesting effect is for NO_x emissions, which correlate inversely with Rh content. This bears out the generally held position that Rh is an important contributor to three-way catalyst activity, especially for NO_x reduction.

Comparison of the fuel consumption figures, which are of course independent of catalyst composition, shows that the range of values is only about 3%, verifying the reliability of our carbon balance determinations.

IV.2 Catalyst Comparisons Under Malfunction Operating Conditions

IV.2.1 HCN

IV.2.1.1 Federal Test Procedure

Table IV-2 shows the HCN results obtained for the 16 FTP runs made at the conditions of varying operating mode and catalyst composition. As discussed in Section III, only 12 of the possible 15 combinations were tested, with four replicates, for a total of 16 runs. The replicates from the FTP, CFDS, 64 kph, and 80 kph tests were combined to provide an estimate of the overall HCN test standard deviation. This value was 2.9.

TABLE IV-1

FTP EMISSIONS AND FUEL CONSUMPTION FOR EXPERIMENTAL CATALYSTS

Normal Vehicle Operation

Relative Noble Metal Amounts	Emissions							Fuel Consumption, lbs/test
	g/km			mg/km				
	HC	CO	NO_x	HCN	NH_3	$SO_4^=$	H_2S	
100% Rh	0.12	1.7	0.21	<1.4	11.7	0.4	<0.1	3.80
17% Rh/83% Pt	0.15	2.1	0.30	<1.4	<6.5	0.6	<0.1	3.68
6% Rh/94% Pt	0.13	2.0	0.41	<1.4	<6.5	0.6	0.3	3.74
100% Pt	0.13	1.9	0.63	<1.4	15.5	0.2	0.2	3.69

Table IV-2

Emission: HCN mg/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	1.3		1.7	1.7	9.5
Idle Correct	2.4				
O_2 Sensor Off	5.2		3.0	2.6	5.5
Idle Enrichened			3.6		8.5
13% Misfire	2.0	2.5		<1.4	8.0
		1.4			

The most striking feature shown in this table are the higher emissions of HCN for the runs made with no catalyst. It appears that all of the catalysts tested, at all three operating modes, actually removed HCN from the exhaust gas. As between the four catalysts themselves, tailpipe emissions appeared similar, except that the all rhodium catalyst showed a higher value for the idle enrichened case. It should be noted also that in nearly every case the FTP emissions of HCN were higher than those measured during normal operation, discussed in Section IV.1. It is not known whether HCN is formed upstream of the catalyst in the combustion chamber or exhaust system.

IV.2.1.2 Congested Freeway Driving Schedule (CFDS)

As in the case of the FTP, the catalysts showed a tendency to remove HCN from the engine out exhaust, as evidenced by the higher values for the no-catalyst case shown in Table IV-3. As between the catalysts, again the all rhodium system was highest, but still did not appear to be a net producer of HCN during this test cycle.

Table IV-3

Emission: HCN mg/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	4.2		1.8	1.1	8.1
Idle Correct	4.6				
O_2 Sensor Off	7.4		1.1	2.0	7.7
Idle Enrichened			2.9		2.6
13% Misfire	5.2	3.3		2.1	7.5
		2.3			

IV.2.1.3 64 KPH Cruise

The results from this cruise mode are more complex than those for the FTP and CFDS cycles discussed in the previous two sections. With the sensor disconnected but the A/F ratio idle adjustment properly set the pure Rh catalyst produced HCN beyond that already present in the raw exhaust, while the low Rh (6%) and pure Pt catalysts removed it. As the exhaust became richer, with the idle A/F adjustment enriched, the pure Rh catalyst produced still more HCN and even the 6% Rh catalyst made some HCN. In this case only the pure Pt catalyst appears to remove HCN. Under misfire conditions all three catalysts removed most of the HCN from the exhaust. These results are shown in Table IV-4.

Table IV-4

Emission: HCN mg/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	7.2		2.3	1.2	5.0
Idle Correct	16.2				
O_2 Sensor Off	39.8		9.2	2.3	3.1
Idle Enrichened			8.3		4.1
13% Misfire	1.4	0.6		<0.8	4.9
		0.8			

IV.2.1.4 80 KPH Cruise

This cruise condition resembled the 64 kph cruise in that the pure Rh catalyst produced HCN with the O_2 sensor disconnected, especially under the enriched mode. In the latter mode the 6% Rh catalyst also made some HCN. All other combinations of catalyst-driving mode removed HCN from the exhaust. These results are shown in Table IV-5.

IV.2.1.5 Idle

Under idle conditions no significant quantities of HCN are produced, either in the raw exhaust or over any of the catalysts at any malfunction mode, as shown in Table IV-6.

Table IV-5

Emission: HCN mg/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% 100% Pt	No Catalyst
O_2 Sensor Off	5.8		3.8	1.4	8.4
Idle Correct	17.2				
O_2 Sensor Off	27.3		11.7	5.0	6.2
Idle Enrichened			11.8		7.1
13% Misfire	3.8	4.6		1.3	10.0
		1.1			

Table IV-6

Emission: HCN mg/min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	<1.0		<0.6	0.6	0.8
Idle Correct	0.6				
O_2 Sensor Off	<0.9		0.8	0.9	0.8
Idle Enrichened			<1.1		<1.1
13% Misfire	<0.8	<0.8		<0.8	0.6
		<0.8			

IV.2.2 NH_3

IV.2.2.1 Federal Test Procedure

As shown in Table IV-7, NH_3 levels are generally much higher than for the normal operating case described in Section IV.1. This appears to apply even to the raw exhaust, although the values do overlap within one standard deviation, and it is not known if the catalysts under stoichiometric operation removed NH_3 from the raw exhaust, or if the engine itself under these malfunction modes produced more NH_3 than the same engine at stoichiometric conditions. Combining the replicated runs from the FTP, CFDS, and 64 and 80 kph cruise modes gave a standard deviation of 32.

The four catalysts under the malfunction modes all increased the NH_3 level in the exhaust, again however, a few of the values overlapped by one standard deviation. Maximum production was shown by the all Rh catalyst, under enriched and misfire conditions. No catalyst composition effect was evident for the correct idle-sensor disconnected case.

Table IV-7

Emission: NH_3 mg/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	103		105	95	50
Idle Correct	100				
O_2 Sensor Off	198		68	142	7
Idle Enrichened			134		20
13% Misfire	214	113		63	24
		68			

IV.2.2.2 Congested Freeway Driving Schedule

This cycle showed much higher levels of catalyst NH_3 production than did the FTP, even though the raw exhaust level was lower. These results are given in Table IV-8. Again the pure Rh catalyst gave the highest levels, during the enriched and misfire operating modes. Also following the FTP pattern was the lack of a catalyst composition effect for the idle correct-sensor disconnected case.

Table IV-8

Emission: NH_3 mg/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	165		158	188	11
Idle Correct	158				
O_2 Sensor Off	279		157	189	7
Idle Enrichened			239		17
13% Misfire	724	195		103	9
		165			

IV. IV.2.2.3 64 kph Cruise

For this cruise test mode the raw exhaust NH levels were lower than observed for the FTP and CFDS cycles, as shown in Table IV-9. Once again the pure Rh catalyst showed the highest levels, similar to those for the FTP, at the enriched and misfire operating conditions. Also, as before, no catalyst composition effect was seen for the idle correct-sensor disconnected case. One difference from the FTP and SET results was a correlation between Rh content and NH_3 production for the enriched case, with pure Rh highest and pure Pt lowest.

Table IV-9

Emission: NH_3 mg/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	138		170	154	4
Idle Correct	193				
O_2 Sensor Off	230		154	55	<2
Idle Enrichened			154		2
13% Misfire	195	99		64	5
		86			

IV.2.2.4 80 kph Cruise

This test mode appeared very similar to the 64 kph case. Unfortunately one data point is missing due to a mechanical problem, but if we assume this value to follow the pattern, then the same conclusions stated for the 64 kph case hold here, although the overall production level is higher. These results are shown in Table IV-10.

Table IV-10

Emission: NH_3 mg/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	431		339	290	5
Idle Correct	309				
O_2 Sensor Off	473		245	131	5
Idle Enrichened			298		2
13% Misfire	---	210		111	5
		189			

IV.2.2.5 Idle

In all cases the NH_3 values were low, about the levels of the stoichiometric case in Section IV.1, with the catalysts showing no increase over the raw exhaust. As in the HCN case, idle production of this unregulated emission is too low to allow further comparisons. These results are found in Table IV-11.

Table IV-11

Emission: NH_3 mg/Min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 84% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	7.2		10.1	8.8	9.9
Idle Correct	6.6				
O_2 Sensor Off	6.2		6.3	7.1	2.7
Idle Enrichened			5.6		<2.0
13% Misfire	6.3	7.0		5.8	4.9
		6.9			

IV.2.3 Carbon Monoxide

IV.2.3.1 Federal Test Procedure

For the two cases with disconnected sensors similar patterns are found, as shown in Table IV-12. The pure Rh catalyst provides the greatest degree of CO conversion, the Pt/Rh catalysts are next and the pure Pt catalyst the lowest. In the enriched case the pure Pt catalyst shows no conversion activity at all, since CO emissions are equal to the no catalyst case. For the misfire mode, all three catalysts provide approximately 60% conversion. The standard deviation calculated from the replicated runs for the FTP, CFDS, and cruise modes is 2.3.

Table IV-12

Emission: CO g/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	10.3		11.6	12.9	21.7
Idle Correct	9.6				
O_2 Sensor Off	23.9		32.2	38.1	37.0
Idle Enrichened			24.2		39.0
13% Misfire	9.6	9.4		9.3	22.7
		9.9			

IV.2.3.2 Congested Freeway Driving Schedule

No clear pattern is discernible for this cycle. The only conclusions apparent are that the Pt catalyst in the sensor-off, enriched mode provides very little CO conversion and that all three catalysts provide about 50% conversion during misfire. These results are given in Table IV-13.

Table IV-13

Emission: CO g/km Cycle: CFDS

Catalyst / Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off, Idle Correct	6.7 7.2		5.8	5.1	12.8
O_2 Sensor Off, Idle Enrichened	13.1		13.1 10.3	17.5	23.4 19.1
13% Misfire	10.6	11.8 9.1		11.2	22.2

IV.2.3.3 64 kph Cruise

With the sensor off but idle A/F control properly adjusted all three catalysts were equivalent, as shown in Table IV-14. However, when the A/F control was enriched, the pure Pt catalyst gave no CO control, while the two Rh containing catalysts were partially effective. Under misfire conditions the three catalysts were equivalent to each other, at about the 70% level.

Table IV-14

Emission: CO g/km Cycle: 64 kph

Catalyst / Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off, Idle Correct	5.8 4.2		5.3	5.4	8.8
O_2 Sensor Off, Idle Enrichened	11.3		12.0 10.3	20.0	18.6 16.2
13% Misfire	4.9	5.2 5.8		5.2	15.7

IV.2.3.4 80 kph Cruise

As shown in Table IV-15, a similar pattern to the 64 kph cruise case is observed for the two O_2 sensor-off modes. However, in the misfire mode the pure Pt catalyst is now more effective for CO control than are the two Rh-containing catalysts.

Table IV-15

Emission: CO g/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	9.9		8.2	6.7	18.1
Idle Correct	7.2				
O_2 Sensor Off	14.5		15.8	22.9	21.4
Idle Enrichened			12.1		15.9
13% Misfire	13.2	15.2 15.3		9.5	24.5

IV.2.3.5 Idle

Under idle conditions, as shown in Table IV-16, little if any CO control was achieved for the two sensor-off cases, except for the pure Rh catalyst with the properly set idle adjustment. Here CO conversion, on average, was about 40%. Under misfire conditions considerably more conversion was achieved, with the pure Rh being most active and pure Pt the least.

Table IV-16

Emission: CO g/Min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	1.7		3.3	2.7	3.4
Idle Correct	2.5				
O_2 Sensor Off	9.6		9.3	9.0	9.5
Idle Enrichened			8.8		10.5
13% Misfire	0.3	0.4 0.4		0.5	3.7

IV.2.4 Hydrocarbons

IV.2.4.1 Federal Test Procedure

As shown in Table IV-17, HC emissions for the two O_2 sensor disconnect modes were least for the pure Rh catalyst and greatest for the pure Pt catalyst. The enriched mode gave higher values than did the case with the proper idle adjustment. During misfire, all three catalysts gave substantial reductions in HC emissions, but the pure Pt was most effective in this case, and pure Rh least effective. The standard deviation for these HC measurements, excluding those at idle, is 0.06.

Table IV-17

Emission: HC g/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.25		0.32	0.39	0.83
Idle Correct	0.25				
O_2 Sensor Off	0.55		0.79	0.85	1.14
Idle Enrichened			0.64		1.11
13% Misfire	3.48	2.85 2.87		2.55	12.48

IV.2.4.2 Congested Freeway Driving Schedule

During this cycle, Table IV-18, the two O_2 sensor disconnect modes showed opposite effects. With the A/F idle adjustment correctly set, the pure Pt catalyst was more effective for HC control than either of the Rh catalysts. However, when the idle A/F setting was enriched, the two Rh catalysts were better. In addition, as expected, the overall control efficiency decreased with enrichment. Under the misfire conditions, the pure Pt catalyst was most effective and the pure Rh the least, similar to the FTP cycle misfire.

IV.2.4.3 64 kph Cruise

As shown in Table IV-19, the two sensor disconnect modes had better HC control over the pure Rh catalyst than the other two catalysts. The pure Pt was worst, and in the enriched case actually gave no control. Under the misfire condition the situation was reversed, with the pure Pt catalyst better than the two Rh-containing catalysts.

Table IV-18

Emission: HC g/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.18		0.16	0.13	0.50
Idle Correct	0.17				
O_2 Sensor Off	0.35		0.38	0.46	0.75
Idle Enrichened			0.28		0.70
13% Misfire	3.26	2.84		2.55	11.32
		2.69			

Table IV-19

Emission: HC g/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.17		0.19	0.20	0.41
Idle Correct	0.12				
O_2 Sensor Off	0.36		0.43	0.52	0.55
Idle Enrichened			0.44		0.52
13% Misfire	2.31	2.47		2.08	6.55
		2.45			

IV.2.4.4 80 kph Cruise

Under this cruise, as shown in Table IV-20, the pattern was mostly similar to the 64 kph cruise, except that under the first malfunction mode, with sensor disconnect but idle adjustment proper, all three catalysts were similar in HC control effectiveness. However, as before, pure Pt was poorest when the idle was enriched, giving very little control, but was best under the misfire condition.

Table IV-20

Emission: HC g/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.32		0.20	0.21	0.52
Idle Correct	0.22				
O_2 Sensor Off			0.42		0.72
Idle Enrichened	0.39		0.42	0.63	0.70
13% Misfire	2.91	3.03		2.45	7.62
		3.24			

IV.2.4.5 Idle

Under idle conditions, little or no control was achieved in the two sensor disconnect modes, with the possible exception of pure Rh for the enriched case. For the misfire case, as before, the pure Pt catalyst gave best HC control. These results are shown in Table IV-21.

Table IV-21

Emission: HC g/Min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.20		0.17	0.20	0.19
Idle Correct	0.18				
O_2 Sensor Off			0.31		0.34
Idle Enrichment	0.26		0.27	0.33	0.32
13% Misfire	0.62	0.44		0.46	2.11
		0.55			

IV.2.5 Nitrogen Oxides

For both of the sensor disconnect modes the pure Rh catalyst gave the highest level of NO_x control, while the Pt-containing catalysts were roughly equivalent to each other. This held true for both cyclic driving modes and the two cruises. It is surprising that lower levels of NO_x emissions were not observed, since the electronic control unit

tended to drive the air-fuel ratio rich when the O_2 sensor was disconnected, especially with the idle adjustment enriched. Two possible explanations for this effect can be proposed. First, under cyclic driving conditions there may be sufficient lean excursions to prevent efficient NO_x reduction at all times. Secondly, there may not be sufficient exothermic heat from CO oxidation under these rich conditions to keep the catalysts at an efficient operating temperature. As was shown in Tables IV-12 to IV-15, only partial CO removal was achieved under malfunction driving modes.

Obviously, the pure Rh catalyst was much more efficient, but whether the poor activity of Pt was due to poorer low temperature activity or less ability to compensate for lean excursions of the air-fuel ratio cannot be determined from this data. The only clear observation is that pure Rh was a better catalyst for NO_x reduction than Pt-containing catalysts when the O_2 sensor was disconnected.

At the misfire condition, however, catalyst activity reversed, with the two Pt-containing catalysts showing better activity, although all three were quite good. This result held true for the CFDS and the two cruises as well.

At idle, all three catalysts controlled most of the NO_x emissions under all operating conditions, and no judgements can be made between them. These results, as well as those for all the test cycle NO_x results, are given in Tables IV-22 to IV-26. The standard deviation for these NO_x measurements, calculated from the replicate FTP, CFDS, and cruise runs, was 0.12.

Table IV-22

Emission: NO_x g/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	NO Catalyst
O_2 Sensor Off	0.38		0.66	0.74	1.40
Idle Correct	0.53				
O_2 Sensor Off	0.26		0.49	0.68	1.22
Idle Enrichened			0.71		1.30
13% Misfire	0.16	0.07		0.05	1.57
		0.07			

Table IV-23

Emission: NO_x g/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.30 0.43		0.70	0.88	1.51
O_2 Sensor Off Idle Enrichened	0.26		0.59 0.87	0.75	1.18 1.61
13% Misfire	0.04	0.01 0.02		0.02	1.36

Table IV-24

Emission: NO_x g/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Rh	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.01 0.03			0.35	0.72
O_2 Sensor Off Idle Enrichened	0.04		0.31 0.23	0.32	0.53 0.50
13% Misfire	0.02	0.01 0.01		0.01	0.88

Table IV-25

Emission: NO_x g/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.00 0.19		0.41	0.56	1.24
O_2 Sensor Off Idle Enrichened	0.39		0.71 0.60	0.60	1.02 1.15
13% Misfire	0.04	0.02 0.00		0.01	1.28

Table IV-26

Emission: NO_x g/Min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.004		0.004	0.003	0.024
Idle Correct	0.004				
O_2 Sensor Off	0.007		0.000	0.001	0.023
Idle Enrichened			0.002		0.022
13% Misfire	0.001	0.002		0.000	0.031
		0.000			

IV.2.6 Sulfate Emissions

The $SO_4^=$ emissions from these runs are presented in Tables IV-27 through IV-31. In addition, since the emissions were so low, Table IV-32 shows them averaged together over the four driving modes, excluding idle, for each catalyst and operating condition. In no case was an emission level exceeding 4 mg/km observed. It can be seen from Table IV-32 that for the two sensor disconnect cases the pure Pt catalyst had the highest emissions, exceeding those from the raw engine exhaust. The pure Rh catalyst, however, in showing the lowest emissions, was lower even than the no catalyst, or raw engine exhaust case. Under misfire conditions the situation was reversed, the pure Rh catalyst having highest emissions, exceeding the raw exhaust case, and the pure Pt the lowest. In all these cases, the Pt-Rh catalysts fell between the two pure catalyst emissions.

Table IV-27

Emission: $SO_4^=$ mg/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	1.0		0.9	1.4	1.4
Idle Correct	0.4				
O_2 Sensor Off	0.4		2.7	2.0	0.9
Idle Enrichened			0.6		0.8
13% Misfire	3.0	1.0		0.6	1.3
		0.4			

Table IV-28

Emission: $SO_4^=$ mg/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.4 0.9		0.8	2.0	1.0
O_2 Sensor Off Idle Enrichened	0.4		1.4 1.0	3.0	0.8 0.7
13% Misfire	1.0	0.8 1.4		0.6	0.6

Table IV-29

Emission: $SO_4^=$ mg/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.0 0.2		0.0	1.0	0.4
O_2 Sensor Off Idle Enrichened	0.0		0.4 0.2	1.6	0.2 0.0
13% Misfire	0.3	0.2 0.1		0.1	0.2

Table IV-30

Emission: $SO_4^=$ mg/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.1 0.2		0.6	1.3	0.3
O_2 Sensor Off Idle Enrichened	0.2		1.4 0.7	3.9	0.3 0.1
13% Misfire	0.6	0.2 1.0		0.1	0.1

Table IV-31

Emission: $SO_4^=$ mg/Min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.0 0.1		0.1	0.0	0.0
O_2 Sensor Off Idle Enrichened	0.0		0.0 0.0	0.1	0.1 0.0
13% Misfire	0.2	0.2 0.2		0.0	0.1

Table IV-32

Emission: $SO_4^=$ g/km Cycle: Average

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	0.42 0.41		0.56	1.42	0.83
O_2 Sensor Off Idle Enrichened	0.31		1.51 0.65	2.60	0.55 0.40
13% Misfire	1.20	0.80 0.59		0.35	0.58

IV.2.7 Hydrogen Sulfide Emissions

While carrying out these runs, ERE also made measurements of H_2S emissions. The results are given in Tables IV-33 to IV-37 and the analytical procedure in Appendix F. The standard deviation for the true replicates, those cases where identical sampling flow rates were used, is 1.27 if all nine true replicate cases are used. However, during FTP testing, during misfire conditions, a pair of replicates gave 7.02 and 1.46 mg/km of H_2S. If this pair is excluded from the calculation, the standard deviation is reduced to 0.59.

Table IV-33

Emission: H_2S mg/km Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.94		0.76	1.69	<0.07
Idle Correct	0.40				
O_2 Sensor Off	0.80		1.25	0.74	15.29*
Idle Enrichened			0.95		0.41
13% Misfire	0.79	7.02		3.78	0.16
		1.46			

Table IV-34

Emission: H_2S mg/km Cycle: CFDS

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	1.69		0.75	1.40	<0.06
Idle Correct	0.72				
O_2 Sensor Off	2.55		2.13	0.68	<0.11
Idle Enrichened			1.02		<0.06**
13% Misfire	8.23	3.35		5.11	0.04
		2.02			

Table IV-35

Emission: H_2S mg/km Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	1.91		0.46	0.58	<0.04
Idle Correct	0.91				
O_2 Sensor Off	3.13		0.41	0.16	<0.08
Idle Enrichened			0.20		0.55**
13% Misfire	0.68	2.77		3.88	0.44
		2.44			

* High value is probably due to unknown experimental mistake.
** Not true replicates - different flow rates which affect limit of detectability.

Table IV-36

Emission: H_2S mg/km Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	3.16		0.44	0.87	<0.04
Idle Correct	2.10				
O_2 Sensor Off	3.03		0.64	0.25	0.07
Idle Enrichened			0.64		0.56**
13% Misfire	0.37	2.72		3.33	0.11
		1.50			

Table IV-37

Emission: H_2S mg/min Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off	0.33		0.52	1.29	<0.04
Idle Correct	<0.05				
O_2 Sensor Off	<0.05		<0.04	0.06	<0.10
Idle Enrichened			<0.09		<0.04**
13% Misfire	0.19	0.12		0.29	0.08
	0.04				

As was shown in Table IV-1, the four experimental catalysts under normal operating conditions gave a maximum of 0.3 mg/km of H_2S for the FTP. Table IV-33 shows that under malfunction conditions increases in H_2S during the FTP are observed, although the absolute emission levels are still low. There appears to be no pattern with catalyst composition changes. As the malfunction mode changes, it appears that misfire can sometimes lead to the highest values, especially if the 7.02 mg/km figure is real. Another suspect number is the 15.29 mg/km observed with no catalyst when the sensor was disconnected and the idle enriched. In no other non-catalyst run, over cyclic or cruise modes, was a value higher than about 0.6 mg/km seen.

The CFDS cycle also has its highest H_2S emissions under misfire conditions, as much as 8.23 mg/km with the pure Rh catalyst. For the other conditions there is again no discernible pattern with catalyst composition.

At cruise, H_2S emissions over the catalysts are also generally increased compared to the engine out H_2S levels. The pure Rh catalyst gives the highest values when the O_2 sensor is disconnected, but the Pt catalyst is highest at misfire conditions. Again, however, the absolute emission levels are low, a maximum of 3.88 mg/km with the pure Pt catalyst at misfire and 64 kph.

At idle, the catalyst H_2S emissions are sometimes higher than the engine-out emissions, but with the exception of the pure Pt catalyst when the idle adjustment was peoperly set, not appreciably higher.

V. References

1. Voorhoeve, R. J. H., et al., "Hydrogen Cyanide Production During Reduction of Nitric Oxide Over Platinum Catalysts," Science, 190, 149, October 10, 1975.

2. Bradow, R. L., and Stump, F. D., "Unregulated Emissions from Three-Way Catalyst Cars," SAE Paper 770369, March, 1977.

3. Ashmead, D. R., et al., "Nitrogen Oxide Removal Catalysts for Purification of Automobile Exhaust Gases," SAE Paper 740249, February, 1974.

4. Griffith, M. G., et al., "Assessment of Automotive Sulfate Emission Control Technology," EPA Report 460/3-77-008, June, 1977.

APPENDIX A

DETERMINATION OF CYANIDE IN SODIUM HYDROXIDE IMPINGER SOLUTIONS USING AN ION-SELECTIVE ELECTRODE

Introduction and Scope

This method is applicable for the determination of cyanide in 0.5M sodium hydroxide impinger solutions. A cyanide ion-selective electrode is used for the measurement.

Summary of Method

The impinger solution is treated with [illegible]cional sodium hydroxide in order to (1) level differences in ion[illegible]stren[illegible] between the scrubber solution and the calibration standards an[illegible]n rease the pH of the scrubber solution to insure that all the h[illegible]en cyanide is converted to cyanide ion. Cyanide is then measured us[illegible] an ion-selective electrode. Sulfide interferes with the method. If it is present, it is removed by treatment of the solution with cadmium carbonate.

Apparatus

(1) Orion 94-06 Cyanide Ion-Selective Electrode, [illegible] equivalent.

(2) Orion 90-01 Single Junction Reference Electrode, or equivalent.

(3) Orion 801A Digital Ion analyzer, or equivalent.

Reagents

(1) 10M sodium hydroxide ionic strength and pH adjustment solution. Dilute 400 g of 50% sodium hydroxide solution to 500 ml with deionized water. Store in a plastic bottle.

(2) 0.5M sodium hydroxide solution.

Cyanide Solutions

NOTE 1: Cyanide is extremely toxic and should be handled using appropriate safety precautions.

Solution 1: 1000 µg CN^-/ml. Prepare by weighing 2.503 g potassium cyanide and making up 1 liter with 0.5M sodium hydroxide.

Solution 2: 100 µg CN^-/ml. Dilute 20 ml of Solution (1) to 200 ml with 0.5M sodium hydroxide.

Solution 3: 10 µg CN^-/m. Dilute 20 ml of Solution (2) to 200 ml with 0.5M sodium hydroxide.

Solution 4: 5 μg CN^-/ml. Dilute 10 ml of Solution (2) to 200 ml with 0.5M sodium hydroxide.

Solution 5: 1 μg CN^-/ml. Dilute 20 ml of Solution (3) to 200 ml with 0.5M sodium hydroxide.

Solution 6: 0.5 μg CN^-/ml. Dilute 10 ml of Solution (3) to 200 ml with 0.5M sodium hydroxide.

Solution 7: 0.1 μg CN^-/ml. Dilute 20 ml of Solution (5) to 200 ml with 0.5M sodium hydroxide.

Solution 8: 0.05 μg CN^-/ml. Dilute 10 ml of Solution (5) to 200 ml with 0.5M sodium hydroxide.

Solution 9: 0.01 μg CN^-/ml. Dilute 20 ml of Solution (7) to 200 ml with 0.5M sodium hydroxide.

NOTE 2: Store all the cyanide solutions in plastic bottles.

NOTE 3: Discard Solutions 3-9 after one week.

Calibration

Refer to the manufacturer's instruction manuals for detailed operating instructions.

(1) Connect the electrodes to the meter. Pipet 20 ml of the 5, 1, 0.5, 0.1, 0.05, and 0.01 μg CN^-/ml cyanide solutions into plastic containers, add 1.0 ml of 10M sodium hydroxide solution, and obtain potential readings. The cyanide solutions should be stirred at a constant rate, and the readings should be taken after the potential stabilizes, ∿5 min. The response of the cyanide electrode drifts and, therefore, the calibration should be checked occasionally. If the electrode drifts excessively, polish it with an Orion 94-82-01 polishing strip and recalibrate.

(2) Obtain a calibration curve by plotting the logarithm of the cyanide concentrations vs. the potential readings. This curve is linear from 0.04 to 5 μg CN^-/ml with a slope of approximately 50 mV per ten-fold change in cyanide concentration. Below 0.04 μg CN^-/ml the curve deviates from linearity.

Procedure

(1) Pipet 20 ml of the scrubber solutions into plastic containers, add 1.0 ml of 10M sodium hydroxide solution and obtain potential readings as indicated above.

If sulfide is present, add approximately 30 mg of cadmium carbonate, stir for 0.5 hr., and filter before obtaining the potential readings.

Calculation

(1) Obtain the cyanide concentration of the scrubber solutions from the calibration curve. Values for cyanide concentrations below 0.04 µg CN^- /ml are only approximate, and conclusions drawn from solutions that are below 0.04 µg CN^- /ml should be tempered.

APPENDIX B

CONSIDERATIONS IN THE MEASUREMENT OF CYANIDE ION USING ION-SELECTIVE ELECTRODES

Introduction

Cyanide ion is measured using an ion-selective electrode by recording the potential developed between this electrode and a reference electrode. The cyanide electrode is composed of a pressed disk of silver bromide and senses cyanide ion by the attack on the electrode to form $Ag(CN)_2^-$. This attack, which results in the dissolution of the electrode, limits its lifetime at high cyanide concentrations, and therefore, the electrode is not generally used in solutions containing more than 5-10 µg CN^-/ml.

Since the electrode response results from attack on the silver bromide disk; AgBr, $K_{SP} = 3 \times 10^{-13}$; to form $Ag(CN)_2^-$, $K_{INSTAB} = 4 \times 10^{-19}$, it follows that any material which chemically attacks the electrode gives rise to a response, and thus interferes with cyanide measurement. Sulfide, Ag_2S, $K_{SP} = 10^{-51}$, is a very serious interferent. Iodide, bromide and chloride interfere to a much less extent; AgI $K_{SP} = 8 \times 10^{-17}$, AgBr $K_{SP} = 3 \times 10^{-13}$, AgCl $K_{SP} = 2 \times 10^{-10}$. The electrode cannot be used in strongly reducing solutions since AgBr would be reduced to elemental silver.

The electrode responds to free cyanide ion. Therefore, the pH of the solution must be sufficiently high, pH >10, so that cyanide ion greatly predominates in solution over hydrogen cyanide, $K_a = 4 \times 10^{-10}$. Furthermore, the presence of materials which complex cyanide ion, such as iron (II) and iron (III) ions; K_{INSTAB} $Fe(CN)_6^{4-} = 10^{-37}$, $Fe(CN)_6^{3-} = 10^{-44}$; must be absent.

Since the response of the electrode is Nernstian, the potential due to cyanide ion is proportional to the logarithm of its activity. Since activity is dependent on ionic strength, the electrode must be calibrated in solutions which have ionic strengths which are similar to those in which cyanide is to be measured.

Scrubbing of Carbon Dioxide Containing Gases

When a sodium hydroxide scrubber is used to remove hydrogen cyanide from carbon dioxide containing gases, (1) the pH of the solution will drop as hydroxide is converted to carbonate and then to bicarbonate eventually reducing the effectiveness of the solution for hydrogen cyanide removal[1], and (2) the ionic strength of the solution will change as the hydroxide, carbonate, and bicarbonate change in the scrubbing solution.

This report is directed to the discussion of a procedure (Attachment I) for the measurement of cyanide in hydroxide scrubbing solutions. The procedure incorporates steps to insure (1) the pH of solutions are sufficiently high so that cyanide ion predominates over hydrogen cyanide, (2) that ionic strength differences between calibration and measurement solutions are leveled, and (3) removal of sulfide from measurement solutions. The response of two ion-selective electrode/reference electrode combinations are also discussed.

Experimental

Cyanide potentials were obtained using an Orion 801A digital voltmeter and an Orion cyanide electrode-Orion single junction reference electrode combination or a Metrohm cyanide electrode (manufactured by Orion to Metrohm specs)-Orion double junction reference electrode combination. The electrodes were allowed to stabilize in cyanide containing solutions before data were recorded. The data that are given in Tables B-1 and B-2 are the average of two to three measurements on the solutions.

Results and Discussion

In order to evaluate the procedure which is employed for cyanide measurements in sodium hydroxide scrubbers used to remove cyanide from carbon dioxide containing gases, see Appendix A, cyanide measurements were made in synthetic model solutions. The procedure was developed on the basis that a 0.5M sodium hydroxide solution is used for scrubbing the gas. Before the measurement of cyanide, the solution is prepared for measurement by adding additional sodium hydroxide to make the solution approximately 1M in sodium ion. This assures that the pH is sufficiently high so that hydrogen cyanide is dissociated into cyanide ion and that the ionic strength of the scrubbing solution is comparable to the calibration solutions, which are prepared in approximately 1M sodium hydroxide.

The model solutions which were used in this study contained 0.005 to 1.0 µg cyanide per ml prepared by dissolving sodium cyanide in (1) 1M sodium hydroxide, (2) 0.75M sodium hydroxide and 0.125M sodium carbonate, and (3) 0.5M sodium hydroxide and 0.25M sodium carbonate. These solutions represent, respectively, the calibration solution, a scrubber solution with 50 percent conversion of hydroxide to carbonate and prepared for cyanide measurement, and a scrubber solution with 100 percent conversion of hydroxide to carbonate and prepared for cyanide measurement. The 100 percent conversion case represents the maximum amount of carbon dioxide that can be contained in a scrubber without the possibility of rendering it ineffective for hydrogen cyanide scrubbing.

The potential measurements obtained on these solutions using an Orion cyanide electrode and a single junction reference electrode are given in Table B-1 and those obtained using a Metrohm cyanide electrode and a double junction reference electrode are given in Table B-2.

The conclusions that can be drawn from the data in the Tables are, that above 0.04 μg CN^-/ml and within the experimental error of the measurement:

(1) The response of the two electrode combinations are equivalent with respect to the potential change observed for a 10-fold increase in cyanide concentration.

(2) The response of the two electrode combinations are independent of the matrices which were studied. This indicates that the procedure that is used for cyanide measurements in scrubber solutions levels the pH and ionic strength effects on cyanide measurements due to dissociation or activity considerations.

(3) Below 0.04 μg CN^-/ml, differences in matrices affect the cyanide response.

(4) The useful limit for both measurement systems are equivalent, approximately 0.04 μg CN^-/ml.

Since the potential measurements were found to be independent of matrix, above 0.04 μg CN^-/ml, they were averaged for each concentration for the electrode systems. These averages are presented in Tables B-1 and B-2, and plotted in Figures B-1 and B-2. As can be seen from the graphs, the calibration is linear above 0.04 μg CN^-/ml. The linear regression lines obtained from the data between 0.04 and 1.0 μg CN^-/ml are indicated on the graphs.

Summary and Conclusions

Using the procedure which is given in Appendix A for cyanide measurements in scrubbers used to remove hydrogen cyanide from carbon dioxide containing gas streams, up to the maximum carbon dioxide content consistent with efficient hydrogen cyanide removal,

- The two electrode systems are equivalent.
- Matrix effects are negligible.
- The cyanide content can be measured to 0.04 μg CN^-/ml with confidence. Below this concentration, large errors are to be expected in cyanide measurements due to matrix effects and deviation of the cyanide response from Nernstian behavior.

TABLE B-1

MEASUREMENT OF CYANIDE USING AN ORION CYANIDE ION-SELECTIVE ELECTRODE AND AN ORION SINGLE-JUNCTION REFERENCE ELECTRODE

	-mV			
CN^-, µg/ml	1.0M NaOH	0.75M NaOH 0.125M Na_2CO_3	0.5M NaOH 0.25M Na_2CO_3	Avg.
0	14.1	3.8	-2.5	---
0.005	16.1	10.6	8.1	---
0.01	22.1	17.8	17.4	---
0.02	29.2	23.0	30.4	---
0.04	41.6	40.1	40.8	40.8
0.06	48.8	48.4	48.9	48.7
0.10	58.8	58.6	64.6	60.7
0.50	94.8	95.4	95.8	95.3
1.00	110.5	112.2	113.2	112.0

50.9 mV
decade

TABLE B-2

MEASUREMENT OF CYANIDE USING A METROHM CYANIDE ION-SELECTIVE ELECTRODE AND AN ORION DOUBLE-JUNCTION REFERENCE ELECTRODE

	-mV			
CN^-, µg/ml	1.0M NaOH	0.75M NaOH 0.125M Na_2CO_3	0.5M NaOH 0.25M Na_2CO_3	Avg.
0	20.3	10.2	1.4	—
0.005	23.1	17.6	13.2	—
0.01	28.8	24.0	22.3	—
0.02	36.3	30.8	35.0	—
0.04	48.7	46.8	45.1	46.9
0.06	56.4	55.6	53.4	55.1
0.10	66.4	65.0	70.0	67.1
0.50	101.0	101.7	101.4	101.4
1.00	116.5	117.1	120.4	118.0

50.7 mV / decade

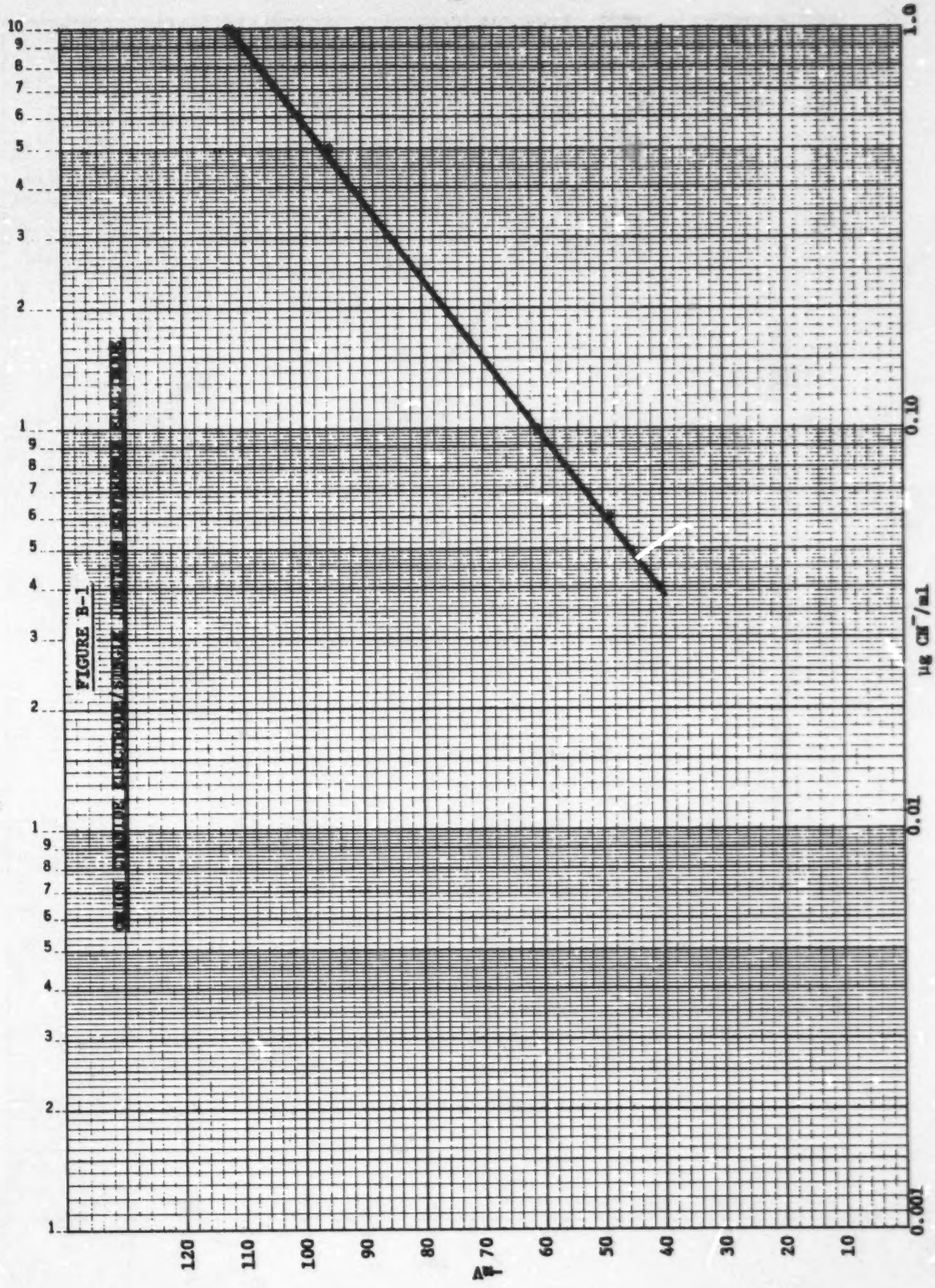
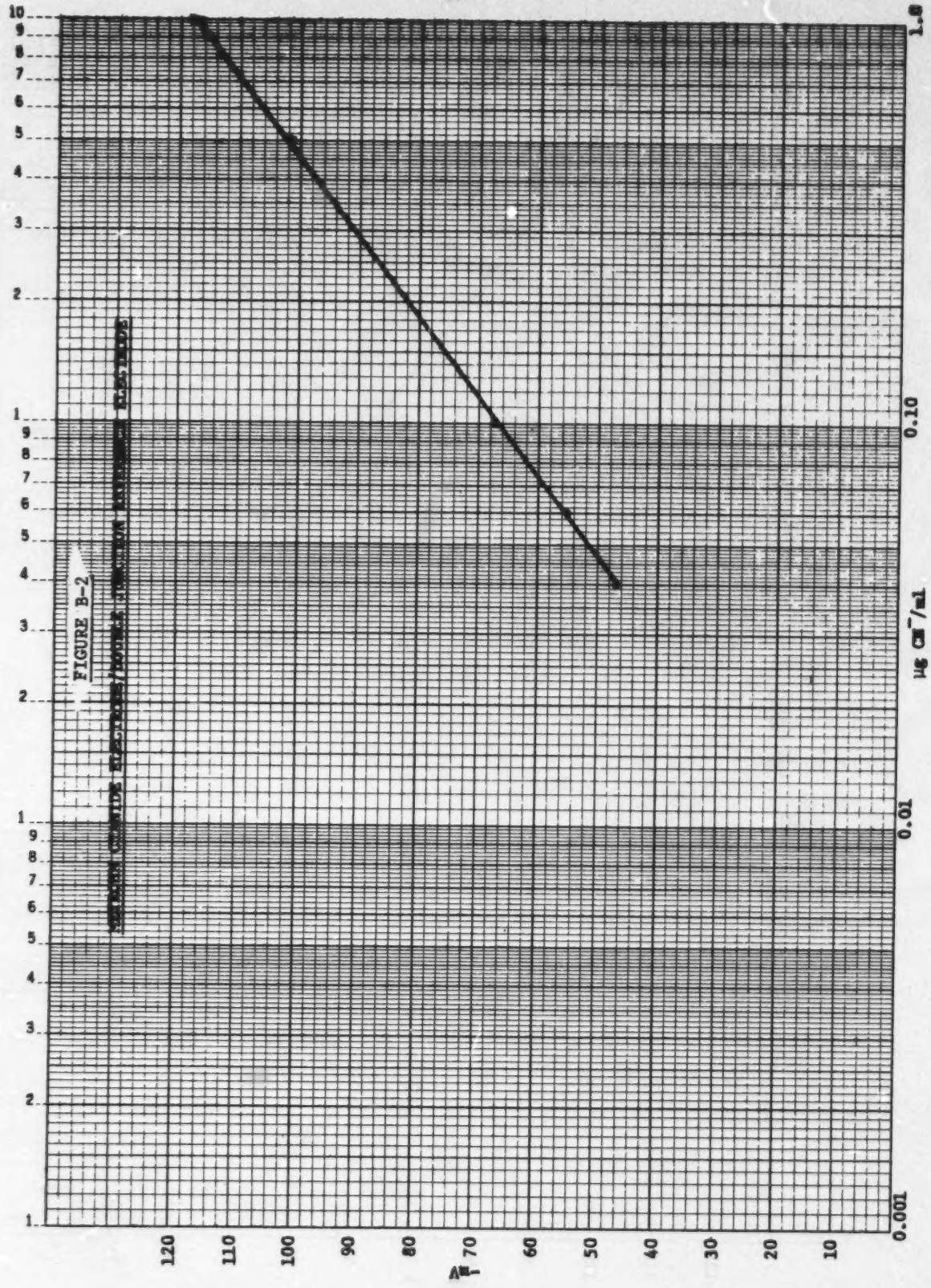

10
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
1.0
0.10
0.01
0.001
µg CH⁻/ml
120
110
100
90
80
70
60
50
40
30
20
10
ΔT

FIGURE B-1


10
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9
8
7
6
5
4
3
2
1
9
8
7
6
5
4
3
2
1
120
110
100
90
80
70
60
50
40
30
20
10
1.0
0.10
0.01
0.001
µg Cm⁻/ml
FIGURE B-2

APPENDIX C

instruction manual

cyanide ion activity electrode
model 94-06

introduction

- required equipment
- before using the electrode
- measurements with a Specific Ion Meter

chemistry of cyanide

- activity and concentration
- effect of pH
- metal ion complexation

cyanide measurements

- activity standards
- general procedure
- activity measurements
- concentration measurements

electrode characteristics

- potential behavior
- electrode life
- precision
- temperature effects
- response time
- interferences

appendices

- I estimating total ionic strength
- II values of 2.3 RT/F

specifications

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Form IM94-06/2701

introduction

The IONALYZER® Cyanide Ion Activity Electrode, Model 94-06, is one of a family of electrochemical sensors developed by Orion Research. Designed to be used like a conventional pH electrode, it has a solid state sensing element and an unbreakable epoxy body which is highly resistant to chemical attack.

At the present time, the 94 series also includes electrodes for fluoride, sulfide, silver, bromide, iodide, and chloride ion. All Series 94 electrodes, which have solid state sensing elements, may be used in a wide variety of aqueous and non-aqueous solutions.

Orion also offers Series 92 electrodes with liquid ion exchanger membranes. Nitrate, calcium, chloride, divalent cation (water hardness), perchlorate, and cupric ion electrodes are currently available in the series. These electrodes are designed to be used in aqueous solutions only.

required equipment

In addition to the electrode, the following equipment is needed to perform cyanide determinations:

IONALYZER Specific Ion Meter, or a pH meter with an expanded millivolt scale

Single Junction Reference Electrode, Model 90-01, or equivalent

Electrode Holder, Model 92-00-01

before using the electrode

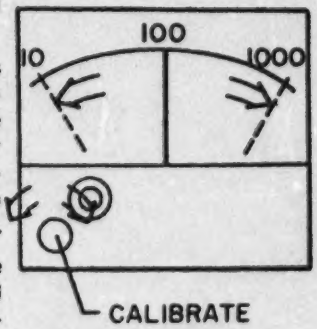
A protective rubber cap is placed over the bottom of the electrode to prevent damage to the sensing element during shipment. Remove the cap before using the electrode. It is advisable to replace the cap when the electrode is not in use.

measurements with a Specific Ion Meter

The upper (red) scale of the Specific Ion Meter is used for direct reading of ion concentration or activity. Readings can be scaled by any power of 10: thus, for example, a center scale reading can be assigned a value of 1.0 ppm or 0.10 M. If the center scale reading is 1 ppm, then the extreme left hand reading is 0.1 ppm, and the extreme right hand reading is 10 ppm.

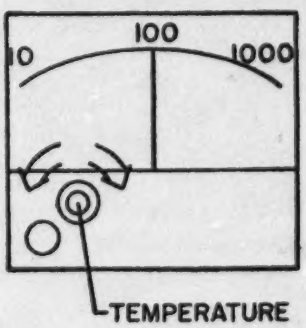
To read cyanide, set the Function Switch to the F^- position.

Place the electrodes in a standardizing solution with a value that is an even power of 10. Turn the calibration control for a center scale reading.

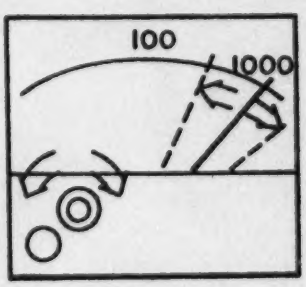


NOTE: Moving the temperature control does not affect a center scale reading.

To obtain the correct slope setting, place the electrodes in a second standard with a value within one decade of the first standard. Now adjust the temperature control until a correct reading is obtained. Move the slope control until the sample temperature is read on the temperature (0-100°C) scale. Now the % of theoretical slope can be read on the slope (80-100%) scale.



The meter is now calibrated and ready for use.



chemistry of cyanide

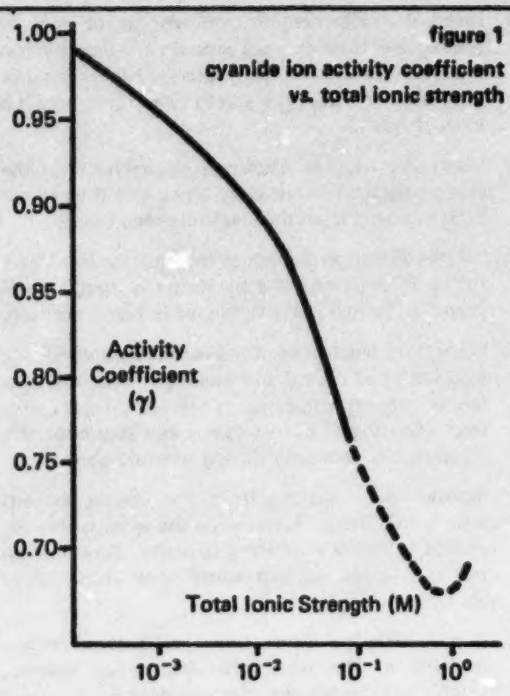


figure 1
cyanide ion activity coefficient vs. total ionic strength

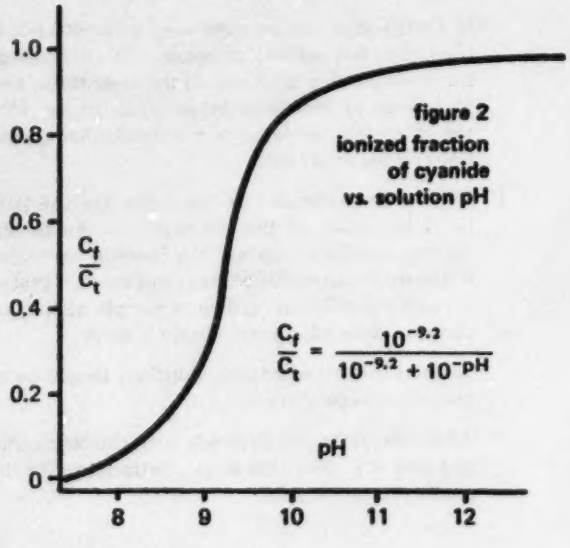


figure 2
ionized fraction of cyanide vs. solution pH

activity and concentration

Cyanide in solution may be present as the free ion (CN^-), or may be complexed to hydrogen or metal ions. The "chemical effectiveness" of the free portion of the cyanide depends on the overall composition of the solution and the solution temperature, as well as on the actual concentration of free, dissociated cyanide ion.

The cyanide electrode responds to the activity (or "effectiveness") of the dissociated cyanide ion. The activity of cyanide ion, rather than the concentration, determines the rate and extent of chemical reactions, and is, in general, a more significant parameter than cyanide ion concentration.

Total cyanide concentration (C_t) consists of both free (C_f) and bound (C_b) ions:

1) $$C_t = C_f + C_b$$

The free cyanide concentration (C_f) is related to the cyanide ion activity (A) by a factor called the activity coefficient (γ):

2) $$A = \gamma C_f$$

The activity coefficient is variable and depends on the total ionic strength of the solution. (See Appendix I.) At low pH's, very little cyanide is in the ionic form, and the effect of total ionic strength is relatively unimportant.

Note that free cyanide (C_f) in this context refers only to the cyanide which is present as the CN^- ion, and should not be confused with the electroplating term meaning all cyanide not bound to metal complexes.

effect of pH

Hydrogen ion complexes cyanide ion to form the weak acid HCN. The greater the hydrogen ion activity, the greater the amount of cyanide ion which is complexed. Figure 2 shows the fraction of free cyanide ion as a function of pH. At pH 8, less than 10% of the cyanide is free; 50% is free at pH 9.2; and at pH 12 virtually all the cyanide is in the form CN^-.

metal ion complexation

Many transition and heavy metal ions (Fe^{++}, Fe^{+++}, Co^{+++}, Ni^{++}, Cu^{+}, Ag^{+}, Cd^{++}, Hg^{++}, etc.) form very stable cyanide complexes. The extent of complexation depends on the relative levels of cyanide and the complexing metal, as well as on solution pH. In acid solutions, there is less metal complexation of cyanide, but greater hydrogen ion complexation.

cyanide measurements

activity standards

Standardizing solutions of fixed pH and total ionic strength are prepared by diluting a 0.1 M cyanide solution with 0.1 M NaOH.

1. Prepare a stock solution of approximately 0.1 M NaOH. Dissolve 4.0 grams of solid NaOH in 1 liter of distilled water. Store in a plastic bottle. Prepare fresh solutions weekly.
2. Prepare a stock solution of 0.1 M CN^-. Dissolve 4.90 grams of reagent grade NaCN in 1 liter of distilled water. (Alternately, 6.51 grams of reagent grade KCN may be dissolved in 1 liter of distilled water.) Store in a plastic bottle. Prepare fresh solutions weekly.
3. Prepare a 10^{-3} M CN^- solution. Pipet 1 ml. of the 0.1 M CN^- solution into a 100 ml. volumetric flask and dilute to the mark with the 0.1 M NaOH solution. This solution must be prepared each day.
4. Prepare a 10^{-4} M CN^- solution by diluting the 10^{-3} M CN^- solution 10:1 with the 0.1 M NaOH solution. If desired, a 10^{-5} M CN^- solution may be made by diluting the 10^{-3} M CN^- solution 100:1 with the stock NaOH solution. These standardizing solutions must also be prepared daily.

NOTE: For activity measurements, cyanide standardizing solutions must be assigned their correct activity values. When using standardizing solutions with a 0.1 M NaOH background, multiply the cyanide ion concentration by 0.77 to obtain the cyanide ion activity value.

general procedure

1. Insert the reference electrode connector into the reference electrode input jack on the Specific Ion Meter or pH meter. Make sure the rubber band or plug used to cover the electrolyte filling hole has been removed.
2. Insert the cyanide electrode connector into the sensing electrode input jack. Make sure the cap has been removed from the electrode membrane.
3. Set the Function Switch of the Specific Ion Meter to the F^- position. If a pH meter is used, set the Function Switch to the expanded millivolt position.
4. Place both electrodes in appropriate standardizing solutions and record the readings. Blot the electrodes between solutions to prevent sample carryover. Stirring of both samples and standards at a fixed rate is necessary during measurement.

   Always blot solutions from the sensing element with a soft tissue. Never wipe the sensing element except to remove adherent deposits. Scratches on the membrane surface cause slow response to changes in ion level.
5. If a Specific Ion Meter is used, calibrate as recommended in the instrument instruction manual. Brief directions are also given on page 3.

   If a pH meter with an expanded millivolt scale is used, plot the activity or concentration values of the standardizing solutions on the logarithmic axis of a piece of semi-logarithmic graph paper. Plot the potentials developed in the standardizing solutions on the linear axis.
6. Place both electrodes in the unknown solution. Read the value of the unknown on the direct-reading specific ion scale of the Specific Ion Meter. If electrode potentials are read out on a pH meter, convert the millivolt reading to sample activity or concentration using the calibration curve.

   Samples and standardizing solutions should be at the same temperature.
7. After use, rinse the electrode with distilled water and blot dry. Store the electrode upright with the protective cap in place.

activity measurements

The electrode responds directly to cyanide ion activity, without regard to sample ionic composition, total ionic strength, pH, or complexing species. To determine the activity in an unknown solution, standardize the electrodes in solutions of known cyanide ion activity and measure the activity of the unknown sample following the directions in the section **general procedure.**

All standardizing solutions and samples should be stirred at about the same rate for good reproducibility.

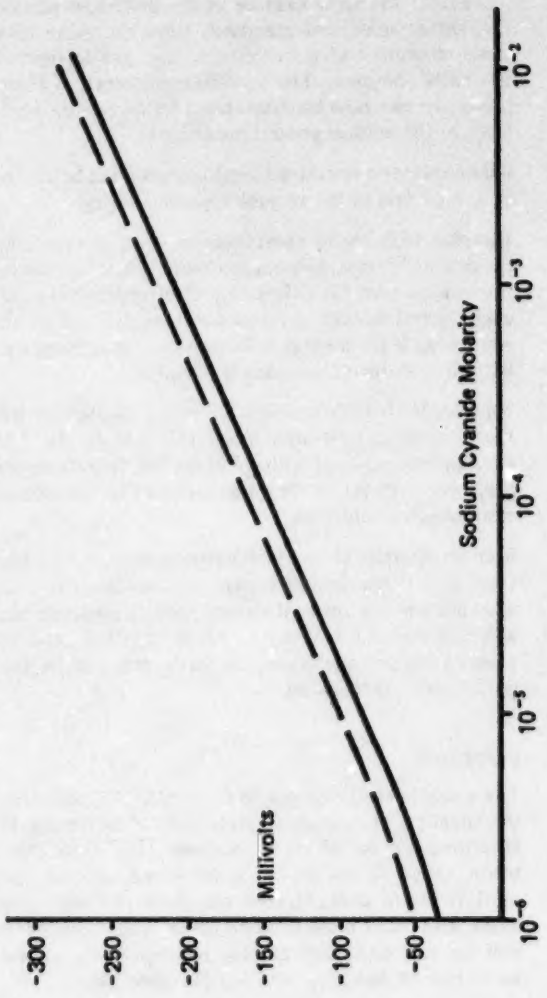
Sample activities can be measured over the range 10^{-3} to 10^{-6} M, and between 10^{-2} and 10^{-3} M on an intermittent basis only. The electrode should not be used in samples with cyanide activites above 10^{-2} M, as excessively rapid corrosion of the sensing element will occur.

The cyanide electrode develops a potential proportional to the logarithm of the activity of the free cyanide ion in the sample solution. At 25°C, the electrode exhibits about a 59 mv change in potential for each tenfold change in cyanide ion activity. Potentials are increasingly positive in more dilute solutions and increasingly negative in more concentrated solutions. Figure 3 (broken line) shows typical potential response of the cyanide electrode to changes in cyanide ion activity. Actual electrode potentials can vary as much as ±20 mv from the values shown, depending on the stirring rate, the reference electrode used, sample temperature, etc.

The Single Junction Reference Electrode, Orion Model 90-01, is recommended.

figure 3

typical electrode response to cyanide ion activity (broken line) and concentration (solid line) (all solutions 0.1 M in NaOH)



concentration measurements

If measurements of total cyanide concentration are required, estimate the total ionic strength and cyanide level of the sample and use **Figure 4** to obtain the recommended sample dilution factor. Prepare pure NaCN standards which bracket the expected value of the unknown and dilute these standards with NaOH in exactly the same manner as the unknown sample. Diluted samples and standards have the same total ionic strength and a sufficiently high pH to destroy the HCN complex. The cyanide concentration of the unknown can now be determined following the directions in the section **general procedure.**

All samples and standardizing solutions must be stirred at a fixed rate to insure good reproducibility.

Samples with metal complexes present, if measured by this technique, give approximate values for the **total free** cyanide (as defined by electroplaters; i.e., all cyanide not bound to metal complexes). Values are approximate since sample dilution can cause some dissociation of the metal-cyanide complex.

Samples with high cyanide levels are diluted to the recommended operating range (10^{-3} M to 10^{-5} M cyanide) as required with 0.1 M NaOH. Standards are prepared with 0.1 M NaOH as outlined in the section **standardizing solutions.**

Standards with high total ionic strengths must be measured in a concentrated background solution so that variations in the original sample ionic strength do not affect the measurement. If 1.0 M NaOH is used to prepare the samples, then standards must also be prepared with 1.0 M NaOH.

titrations

The cyanide electrode can be used as an end point for the titration of cyanide solution with silver nitrate. If titrations are to be done routinely, the silver electrode, Orion Model 94-16, is preferred, as it can be used in more concentrated solutions and will give larger end-point breaks. Using either electrode, there will be two end-point breaks, corresponding to the formation of $Ag(CN)_2^-$ and AgCN respectively.

electrode characteristics

potential behavior

The sensing element of the cyanide electrode is a solid mixture of inorganic silver compounds. This membrane is an ionic conductor which allows silver ions to pass between the sample solution and the internal reference solution, which is kept at a fixed silver ion level. The distribution of silver ions between the two solutions develops a potential which depends on the silver ion activity in the sample solution:

3) $$E = E_a + 2.3\frac{RT}{F}\log A_{Ag^+}$$

where: E = the measured total potential of the system

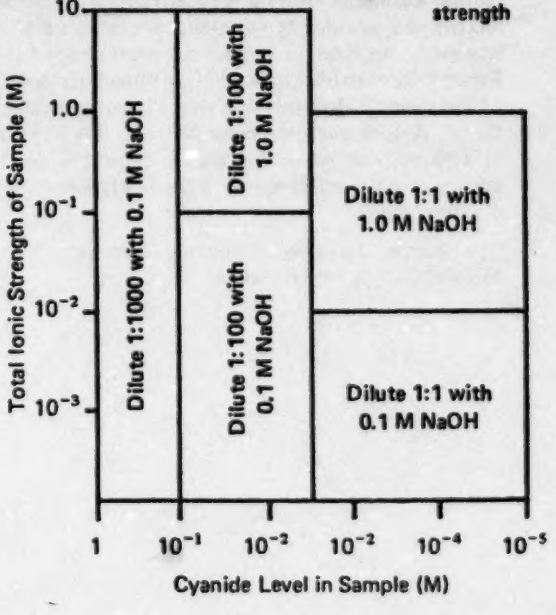
E_a = the portion of the total potential due to choice of reference electrodes and internal solutions

2.3 RT/F = Nernst factor (59.16 mv at 25°C): R and F are constants, and T is the temperature in degrees Kelvin

A_{Ag^+} = the silver ion activity in the sample solution

figure 4

recommended sample dilution vs. sample total ionic strength



The operation of the electrode depends on the reaction of cyanide ion with sparingly soluble silver salts from the membrane surface:

4) $AgX + 2CN^- \rightarrow Ag(CN)_2^- + X^-$

The ions (X^-) released by this reaction fix the activity of silver ion at the membrane surface through the solubility product relationship:

5) $$A_{Ag^+} = \frac{K_{sp}}{\upsilon A_{X^-}}$$

where K_{sp} is the solubility product of the silver salt and υ depends on the stirring rate. Substitution in Equation (3) yields:

6) $$E = E_a + 2.3\frac{RT}{F}\log\frac{2K_{sp}}{\upsilon A_{CN^-}}$$ or:

7) $$E = \left[E_a + 2.3\frac{RT}{F}\log\frac{2K_{sp}}{\upsilon}\right] - 2.3\frac{RT}{F}\log A_{CN^-}$$

When the temperature does not vary and the stirring rate is kept reasonably constant, the terms in brackets are constant and can be defined by a new constant E_b:

8) $$E = E_b - 2.3\frac{RT}{F}\log A_{CN^-}$$

electrode life

Operation of the electrode depends on the slow solution of one of the electrode membrane components (see the section **potential behavior**). Ultimately the membrane will erode to a point where satisfactory operation is no longer possible. Lifetimes decrease at high sample cyanide levels and at high rates of stirring. At moderate stirring rates, the electrode should last for several hundred hours of continuous operation at a 10^{-3} M cyanide ion level. At 10^{-5} M cyanide levels the electrode should operate for over four months. The electrode can be used in NaOH solutions as concentrated as 5 M, and in mixed water and water-soluble organic solvents.

precision

The electrode will detect low levels of cyanide ion; however, since it is a logarithmic device, it cannot be used to detect very small changes in cyanide ion activity at high cyanide levels. Factors such as electrode temperature, drift, noise, and stirring rate limit the precision. With frequent calibration, measurements should be reproducible to ±15% of the cyanide ion activity of the sample solution.

temperature effects

Since electrode potentials are affected by changes in temperature, samples and standardizing solutions should be close to the same temperature. The absolute potential of the reference electrode changes slowly with temperature because of changes in the solubility equilibria on which the electrode depends. The slope of the cyanide electrode also varies with temperature, as indicated by the factor 2.3 RT/F in the Nernst equation. Values of the Nernst factor are given in Appendix II.

response time

With stirring, typical response varies from several seconds in 10^{-3} M cyanide ion solutions to several minutes around the limit of detection. Response is more rapid when going from dilute to concentrated solutions than in the other direction.

Deposits which accumulate on the sensing element degrade response time and should be removed.

interferences

The electrode will malfunction if ions which form very insoluble salts of silver are present at sufficiently high levels to form a layer of silver salt on the membrane surface. In addition, the electrode must not be placed in strongly reducing solutions, such as photographic developer, which form a layer of silver metal on the electrode membrane. The electrode can be restored to normal operation by wiping off the membrane surface.

Table 1 gives the maximum allowable concentration of the more common interfering ions, expressed as the ratio of the interfering ion concentration to the sample cyanide concentration. If the ratio is less than that listed in the table, neither the accuracy of the measurement nor the surface of the electrode membrane will be affected. The more concentrated the cyanide solution to be measured, the higher the allowable concentration of interfering ions.

Hydrogen ion and many metal ions complex cyanide. Although the electrode is not affected by these ions, their presence lowers the level of free cyanide ion in the sample.

Sufficiently high concentrations of species which form extremely stable complexes with silver (NH_3, $S_2O_3^=$) also interfere with measurements and result in the reading of higher values of cyanide ion activity than actually exist in the sample. Intermittent exposure to high levels of these species will not, however, damage the electrode.

table 1

maximum allowable ratio of interfering ion to cyanide ion (concn. of interfering ion/concn. CN^-)

Interference	Maximum Ratio
Cl^-	10^6
I^-	0.1
Br^-	5×10^3
$S^=$	must be absent

To illustrate the use of **Table 1**: What is the maximum allowable Br^- concentration at which a 3.3×10^{-5} M NaCN solution may be measured?

The maximum allowable ratio of Br^- to CN^- is given in Table 1 as:

$$\text{Max. Ratio} = 5 \times 10^3$$

Therefore:

$$\text{Max. } Br^- = 5 \times 10^3 (3.3 \times 10^{-5}) \text{ M Br}$$
$$= 1.6 \times 10^{-1} \text{ M } Br^-$$

appendices

appendix I

estimating total ionic strength of mixed electrolytes

The total ionic strength of a solution is given by the equation:

$$\text{Ionic Strength} = \tfrac{1}{2} \sum Z_i^2 \, C_i$$

that is, the concentration of each and every ion in the solution (C_i) is multiplied by the corresponding square of the charge on the ion (Z_i), and the sum of these products is divided by 2.

For example, a solution of the following composition:

0.05 moles per liter NaCN
0.20 moles per liter K_2SO_4
0.15 moles per liter NaOH

has a total ionic strength calculated as follows:

ion	Z_i^2		C_i		
Na^+	1	x	0.05 + 0.15	=	0.20
K^+	1	x	0.20 + 0.20	=	0.40
$SO_4^=$	4	x	0.20	=	0.80
OH^-	1	x	0.15	=	0.15
CN^-	1	x	0.05	=	0.05
				total =	1.60

$$\text{Ionic Strength} = \frac{1.60}{2} = 0.80 \text{ M}$$

appendix II

values of 2.3 RT/F in millivolts

t (°C)	2.3 RT/F	t (°C)	2.3 RT/F
0	54.20	30	60.15
10	56.18	40	62.13
20	58.16	50	64.11
25	59.16	100	74.04

specifications

activity range	10^{-2} M to 10^{-6} M CN^-
recommended operating range	10^{-3} M to 10^{-5} M CN^-
temperature range	0° to 100°C
pH range	pH 0 to pH 14
electrode body	acid, base, and solvent resistant epoxy
electrode resistance	less than 30 megohms
electrode life	about 200 hours in a 10^{-3} M cyanide solution: about 1000 hours in a 10^{-5} M cyanide solution
interferences	sulfide must be absent: iodide level must be one-tenth the cyanide level
size	electrode is 6" long, with a 30" cable and a U.S. Standard electrode connector: longer cables available on special order
storage	electrode must be stored dry: soaking before use is not required
minimum sample size	10-20 ml. in a 50 ml. beaker

APPENDIX D

DETERMINATION OF AMMONIA IN SULFURIC ACID IMPINGER SOLUTIONS USING A GAS-SENSING ELECTRODE

Introduction and Scope

This method is applicable for the determination of ammonia in 0.2% sulfuric acid impinger solutions. A gas sensitive ammonia electrode is used for the measurement.

Summary of Method

The impinger solution is treated with sodium hydroxide to convert ammonium ion to ammonia. Ammonia is then measured using a gas sensitive ammonia electrode.

Apparatus

(1) Orion 95-10 Gas Sensitive Ammonia Electrode, or equivalent.

(2) Orion 90-01 Single Junction Reference Electrode, or equivalent.

(3) Orion 801A digital Ion Analyzer, or equivalent.

Reagents

(1) 10M sodium hydroxide solution. Dilute 400 g of 50% sodium hydroxide solution to 500 ml with deionized water. Store in a plastic bottle.

Ammonia Solutions

Solution 1: 1000 µg NH_3/ml. Prepare by weighing 3.140 g ammonium chloride and making up to 1 liter with deionized water.

Solution 2: 100 µg NH_3/ml. Dilute 20 ml of Solution (1) to 200 ml with deionized water.

Solution 3: 50 µg NH_3/ml. Dilute 10 ml of Solution (1) to 200 ml with deionized water.

Solution 4: 10 µg NH_3/ml. Dilute 20 ml of Solution (2) to 200 ml with deionized water.

Solution 5: 5 µg NH_3/ml. Dilute 20 ml of Solution (3) to 200 ml with deionized water.

Solution 6: 1 µg NH_3/ml. Dilute 20 ml of Solution (4) to 200 ml with deionized water.

Solution 7: 0.5 μg NH_3/ml. Dilute 20 ml of Solution (5) to 200 ml with deionized water.

Solution 8: 0.1 μg NH_3/ml. Dilute 20 ml of Solution (6) to 200 ml with deionized water.

Calibration

Refer to the manufacturer's instruction manuals for detailed operating instructions.

(1) Connect the electrodes to the meter. Pipet 20 ml of the 100, 50, 10, 5, 1, 0.5, and 0.1 μg NH_3/ml solutions into plastic containers. Add 0.3 ml of 10M sodium hydroxide solution just before obtaining potential readings. The solutions should be stirred at a slow, constant rate, and the readings should be taken after the potential stabilizes.

(2) Obtain a calibration curve by plotting the logarithm of the ammonia concentration vs. the potential readings.

Procedure

(1) Pipet 25 ml of the scrubber solutions into plastic containers, add 0.3 ml of 10M sodium hydroxide solution, and obtain potential readings as indicated above.

Calculation

(1) Obtain the ammonia concentration of the scrubber solutions from the calibration curve.

APPENDIX E

Fuel Economy

Table E-1

Emission: Fuel Lbs. Cycle: FTP

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	3.59 3.63		3.58	3.55	3.59
O_2 Sensor Off Idle Enrichened	3.81		3.89 3.81	3.76	3.74 3.96
13% Misfire	3.89	3.80 3.81		3.94	3.98

Table E-2

Emission: Fuel Lbs. Cycle: SET

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	3.23 3.52		3.22	3.36	3.31
O_2 Sensor Off Idle Enrichened	3.57		3.49 3.59	3.40	3.38 3.67
13% Misfire	3.74	3.51 3.75		3.85	3.82

Table E-3

Emission: Fuel Lbs. Cycle: Idle

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	1.49 1.44		1.57	1.50	1.36
O_2 Sensor Off Idle Enrichened	1.58		1.57 1.53	1.46	1.45 1.47
13% Misfire	1.59	1.44 1.42		1.42	1.51

Table E-4

Emission: Fuel Lbs. Cycle: 64 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	3.86 3.74		3.79	3.90	3.77
O_2 Sensor Off Idle Enrichened	3.95		3.99 3.78	4.15	4.02 3.91
13% Misfire	4.35	4.41 4.19		4.31	4.23

Table E-5

Emission: Fuel Lbs. Cycle: 80 kph

Catalyst/ Malfunction	100% Rh 0% Pt	17% Rh 83% Pt	6% Rh 94% Pt	0% Rh 100% Pt	No Catalyst
O_2 Sensor Off Idle Correct	5.46 5.27		5.14	5.33	5.53
O_2 Sensor Off Idle Enrichened	5.56		5.62 5.35	5.51	5.47 5.33
13% Misfire	6.29	6.22 6.28		6.20	6.22

APPENDIX F

PROCEDURE FOR THE DETERMINATION OF HYDROGEN SULFIDE IN AUTOMOTIVE EXHAUST USING THE METHYLENE BLUE METHOD

Reagents

1. Acetate Buffer - dissolve 54.9 g of zinc acetate [$Zn(C_2H_3O_2)_2 \cdot 2H_2O$] and 8.2 g of sodium acetate ($NaC_2H_3O_2$) in deionized water. Dilute to one litre with deionized water.

2. Amine Solution - dissolve 0.93 g of N,N-dimethyl-p-phenylene diamine sulfate in 75 cc of deionized water. Cautiously, add 187 cc of conc. H_2SO_4, cool, and dilute to 1 litre with deionized water.

3. Ferric Solution - dissolve 120.6 g of ferric ammonium sulfate in 750 cc of deionized water. Add 27 cc of conc. H_2SO_4, cool, and dilute to 1 litre with deionized water.

4. Formaldehyde Solution - dilute 10 cc of formaldehyde (37%) to 100 cc with deionized water.

Standardization and Calibration

1. Weigh approximately 8 g of $Na_2S \cdot 9\ H_2O$ in a beaker. Rinse the crystals with deionized water before dissolution in a nitrogen purged one litre volumetric flask. Dilute to the mark with deionized water.

2. Dilute 10 cc of this solution to one litre in another nitrogen purged volumetric with deionized water. This solution contains approximately 10 ppm sulfide.

3. Using a 5 cc micro buret, add 0.1, 0.25, 0.5, 1, 2, 3, and 5 cc of the sulfide soln to 100 cc volumetric flasks, which contain 10 cc of the acetate buffer. Rinse down the added sulfide with approximately 40 cc of deionized water. Swirl to insure mixing. Prepare a blank of the acetate buffer.

4. Immediately add 50 cc of the sulfide soln to each of 3 Erlenmeyer flasks containing 10 cc of the acetate buffer and mix. Prepare two blanks containing the buffer and 50 cc deionized water.

5. Pipet 5 cc of a 0.01N I_2 soln to one of the Erlenmeyer flasks. Add 10 cc of conc. HCl and titrate to a starch end point with standardized 0.01 N sodium thiosulfate using a 5 cc micro buret. Repeat this procedure with the remaining flasks.

6. Calculate the concentration of the sulfide solution and the total micrograms of sulfide added to each calibration flask.

7. To the sulfide blank calibration flask, add 1 cc of the formaldehyde soln and mix. Add 10 cc of the amine solution down the side of the flask. Taking care not to introduce air bubbles, swirl the flask gently to mix the reagent. Add 2 cc of the ferric solution and swirl an additional 30 seconds. Dilute to the mark with water and place in the dark. Repeat this procedure with the other flasks.

8. After 15 minutes, measure the absorbance on a spectrophotometer at 667 nm in 5 cm cells against water.

9. Plot the absorbance of each flask against µg sulfide contained on linear graph paper.

Note: The calibration curve may not necessarily follow Beer's Law (i.e., not a straight line). In that case, plot the best curve between the points.

Procedure for Samples

1. Samples are collected by passing a measured amount of gas at a determined rate through specially designed scrubbers containing 10 cc of the acetate buffer and 40 cc deionized water.

2. To one of the samples add 1 cc of formaldehyde solution and mix well. Add 10 cc of the amine solution through the inlet tube of the scrubber. Mix the reagent by drawing the samples up and down through the inlet tube. This can be done using a rubber suction bulb. Add 2 cc of the ferric solution through the inlet tube and repeat the mixing procedure described for 30 seconds. Quantitatively, transfer the scrubber contents to a 100 cc volumetric flask and dilute to the mark. Set the flask in the dark. Repeat with the remaining samples.

3. After 15 minutes, measure the absorbance at 667 nm in 5 cm cells against water.

4. Read from the calibration curve the total µg of sulfide present in the sample.